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## SECTION I - Airborne Contamination and Toxicity

Prior to discussion of the problems and techniques encountered in atmosphere control on submarines, it is worthwhile to consider the underlying situation. Certain assumptions may be made about a closed environment which are useful in approaching the problem of control of the various atmospheric constituents. These include:

1. Once sealed, all constituents added to the atmosphere derive from endogenous sources.
2. Removal must be accomplished by means within the environment.
3. With some degree of accuracy, the rate of evolution and removal may be predicted. This is particularly true of such materials as the physiologic gases.

Accepting these assumptions, one may establish a basic mathematical equation which may be utilized to determine the quantity present:

Rate of Change of Component = Introduction Rate - Removal Rate

Within the framework of this formulation, one must consider which of several conditions exists prior to its application. The general categories may be summarized as follows:

1. Constant introduction; constant removal
2. Constant introduction; variable removal
3. Variable introduction; constant removal
4. Variable introduction; variable removal

Any one of the categories may be expected to exist with respect to atmospheric contaminants. The dynamics of removal of a single large quantity of freon will vary widely from that of constantly generated carbon dioxide.

To bring this to a practical level, one must next consider the question of concentration. Before one may become involved in matters of removal, he must first decide at what level it is necessary to hold the concentration, if at all. For most airborne materials and gases with which one must be concerned, a maximum allowable concentration (MAC) has been established. Thus, we are told within what limits we must keep CO<sub>2</sub>, CO, and other materials we expect to find in the submarine atmosphere.

Then, all that is necessary is to be sure that the rate of removal exceeds or at least equals the rate of generation. In the latter case, with equal generation and removal, the equilibrium established must be at a level at or below the MAC. Thus, in consideration of each component of the normal atmosphere and of atmospheric contaminants, the rates of production and removal as well as the desirable concentration must be evaluated.

#### Maximum Allowable Concentration (MAC):

It has been found expedient to arrive at a maximum allowable concentration (MAC) for a great many different compounds. This developed through an increasing awareness in industry, industrial medicine, and in claims courts of the hazardous and debilitating effects of various chemicals on human physiology. Many values are at best estimates and are based on the prima facie evidence that no particular effect on people has been detected at values below the value cited. In addition, MAC's have always been based on a limited continuous exposure, usually on eight hour working day. Except for a few compounds, this allows any buildup in the body to dissipate before another exposure and, over weekends, many hours to reduce any body concentration to very low values.

Our submarines are being built with a long-term submergence capability. An individual exposed to a unique atmospheric contaminant for sixty days or more cannot be considered in the same light as one with intermittent short exposures. Nor can a MAC valid in the latter case be expected necessarily to be valid in the continuous exposure situation. There is, unfortunately, extremely little information available on long-term exposures and, indeed, the usual research sources of such material are loathe to accept such projects which will tie up equipment for long periods of time. To a certain extent, therefore, it is necessary to extrapolate (on a non-linear basis) known MAC values from the 24 hour/day long-term exposure conditions. One does this reluctantly but necessarily.

One must differentiate compounds into two broad categories in discussing the applicability of MAC's to closed environmental situations. There are those we expect to find on a submarine. As indicated previously, MAC's have been improvised for these. On the other hand, there are those we do not expect to find routinely on a submarine, but whose presence could pose a serious threat to health. With those expected materials, one must either control their generation, provide for their removal, live with them, or give up long-term submarine operations. The other group might well be called

emergency gases because their appearance represents an emergency of variable degree. These materials are rarely seen and there does not seem to be fixed or steady source. These gases may be very toxic and action must be based on their intensity and absolute toxicity. Long-term exposure MAC's have not been obtained for this group. With confirmation of the presence of one of these gases and with appraisal of its toxicity, both from literature and symptomatology, several courses of action are possible:

1. If source can be found and stopped and levels are well below standard MAC's, no further action is necessary.
2. If source can be found and stopped, even if the local reading is quite high, it is possible to wait for dilution throughout the boat. If the reading throughout is of the order of the Industrial MAC, one may watch it for eight hours for evidence of diminution. If it continues to diminish and no symptoms develop among personnel, no further action is necessary.
3. If the initial concentration is up to a dangerous level; if the source cannot be quickly found and stopped; or if personnel develop symptoms traceable to the material one must recommend either surface ventilation or manifold breathing, whichever is more quickly available.
4. If the operational or tactical situation is not one requiring continued submergence, it is preferable to surface ventilate when any appreciable quantity of material is discovered in the submarine.

It will thus be evident that the concept of MAC is one subject to interpretation, depending on the circumstances under which it must be applied. If one bears in mind that the industrial MAC's represent, for the most part, values derived from many years of observation (including long-term effects), it should be self-evident that our arbitrarily assigned values for long-term exposure are subject to constant revision (usually downward).

### Sources of Atmospheric Contamination

In the closed environment of nuclear submarines there are many sources of atmospheric contamination. Some materials are hazardous because they are inately toxic even in low concentration; some because of low vapor pressure; some occur as gases; and some as aerosols. In considering the source of any given contaminant, those factors contributing to its toxicity must also be evaluated.

It is true but not helpful to state that any gas or chemical compound can be toxic under proper circumstances. One must at the outset accept a compromise between the ideal and the practical. We are not doing our job if we pose so many potential or hypothetical problems as to make submarine operations per se untenable. On the other hand, with a known toxic agent that is either susceptible to substitution or (in some cases) elimination, we cannot accept complacency on the sole basis of convenience. It is, therefore, necessary to exercise judgment and discrimination when investigating the source of an atmospheric contaminant. There is listed below a number of representative sources of contaminants. It is not intended to be complete and will vary widely from submarine to submarine:

Acrolein	Frying
Aerosols, various	Smoking, respiration
Airborne ions	ESP sparking
Aldehydes	Treating elect. insul.
Aliphatic-aromatic hydrocarbons	Paints-solvent thinners-fuel
Arsine-stibine	Battery gassing
Carbon monoxide	Smoking
Chlorinated hydrocarbons	Solvents - Carbon tetrachloride, etc.
Freon	Refrigeration; shaving cans
Glycols	Water based paints
Hydro-chloric & fluoric acid	CO burner from freon
Hydrogen peroxide	Torpedoes
Menthol	Shaving lotions, etc.
Metal fumes	Burning - welding
Methane	Organic decomposition
Methanol	Duplicator chemicals
Mercury	Batteries - thermometers
Nitrous gases	Diesel exhaust
Ozone	Sparking
Phosphorous compounds	Lubricants and fuel
Sulfur compounds	Lubricants and fuel
Sulphur dioxide	Diesel exhaust
Sulphuric acids	Battery mist
Others	Special equipment and uses

The wide scope of sources for toxic materials may be recognized. One must maintain a high order of suspicion. There is little doubt, for example, that the use of hydrocarbon solvents makes the job of keeping machinery and surfaces much easier than does the use of soaps and detergents. Oversight, inadvertence, and oftentimes design will cause a submarine to go to sea with these materials on board despite control programs to prevent this.

That a material is forbidden cannot be taken as proof that it is not used. Individuals may well introduce materials innocently because they do not know the constituents. Spray cans with shaving soap and the like are charged with freon gas which is not considered safe aboard submarines. Other examples, such as shoe polish, come readily to mind.

In general one cannot flatly interdict a substance's being on board without strong evidence of its hazard. The argument, "We've used this on submarines for twenty-five years without hurting people," may be completely specious (and oftentimes is) but is nonetheless difficult to counter. The proper approach again is through compromise. If one can offer a substitute, even if less efficient, with markedly less toxic hazard, the chances of acceptance are greatly increased.

The development of submarines is based in large part on concurrent progress in technology. The latter embraces a continuing search for complex chemical compounds with special characteristics. Such compounds will oftentimes suddenly appear unobtrusively as a part of new or improved equipment. Not only will the presence of the compound not be advertized but once discovered, information concerning its toxicity or even its chemical constituency may be extremely difficult to obtain from manufacturers because of the proprietary nature of the material. When such materials occur without accompanying or amplifying information, a query should be made through the chain of command to cognizant codes in the Bureau of Medicine and Surgery and the Bureau of Ships (or Weapons, if applicable). The chain of command should be utilized in every case to assure dissemination of information regarding the problem on the Squadron and Force level.

## Toxicity

The toxicity of any given material depends on a large number of factors. Those concerning the physical characteristics of the compound or element have been mentioned. The physiological variants which affect specific toxicity involve the mode of entry, distribution within the body, organs or systems affected and, in some cases, critical concentrations within the body to result in any given response. Generally, the primary concern on submarines is with the respiratory mode of entry, but obviously skin, mucous membrane and digestive routes may be important.

There are several ways of classifying toxic materials. The following is one based on a physiological basis:

- A. Irritants - corrosive or vesicant. The concentration factor is the governing one
1. Upper respiratory tract: e.g. aldehydes, acrolin, ammonia, sulfur dioxide.
  2. Upper respiratory tract and lung tissue: e.g. halogens, ozones, phosphorous trichloride
  3. Terminal bronchioles and alveolae
- B. Asphyxiants - interference with oxidation of tissues
1. Simple asphyxiants: e.g. carbon dioxide, helium, methane, nitrogen
  2. Chemical asphyxiants: e.g. carbon monoxide, cyanides, anilines, nitrobenzene, hydrogen sulphide
- C. Anaesthetics and Narcotics - central depressing effect is pre-dominant.
1. e.g. actylene hydrocarbons, olefins, paraffins, aliphatic ketones and alcohols, some esters.
- D. System poisons
1. Damage to one or more visceral organs: e.g. halogenated hydrocarbons.
  2. Damage to haemopoietic system: e.g. benzene, phenols, toluene, xylene
  3. Nerve poisons: e.g. carbon disulphide, methanol
  4. Toxic metals: e.g. lead, mercury, cadmium, antimony, beryllium
  5. Other inorganics: e.g. arsenicals, silenium, sulfides, fluorides
- E. Particulate matter other than systemic poisons
1. Fibrosis-producing dusts: e.g. silica, asbestos
  2. Inert dusts: e.g. carbon, emery
  3. Allergenic dusts: e.g. pollen, resins
  4. Irritants: acids, alkalies
  5. Bacteria and other microorganisms

(from Patty)

The lungs being a primary concern as a mode of entry, the following values are potentially useful in determining to what an individual breathing a contaminated atmosphere is liable to be subjected:

Respiratory rate = 10-20/min (avg. 15)  
Total lung capacity = 5-6 liters  
Vital capacity = 4.5 liters  
Tidal volume = 0.5 liters  
Respiratory minute volume (RMV) =  
    Complete rest = 6 liters  
    Heavy work = liters  
                    (Diving Manual)

Haemodynamics also must be considered, as the dissemination of substances from the lungs throughout the body depend upon this movement.  
Normal stroke volume - 60-70 ml.  
Normal pulse rate - 68-72 /min.  
Minute volume - 4-5 liters

A great many conditions, including work, thermal stress, emotional stress, etc., can increase both the respiratory and cardiac minute volumes. An individual who is doing heavy work or one who becomes excited in a contaminated atmosphere is more susceptible to earlier and more severe symptoms of poisoning than one who is at rest.

#### Calculations

In using and reporting toxicological data, there are several calculations it may be necessary to make. In the reporting of atmospheric gases on board submarines, it makes little difference in instances where they are reported as absolute or effective (partial pressure) percentages. It is necessary only to have it clearly understood by all concerned how the measurement is to be made. Also, despite the fact that reporting in terms of partial pressures is in many ways more satisfactory, it is usually much easier for the medically unsophisticated to understand percentages in reporting.

Boyle's Law - If the temperature is kept constant, the volume of a gas will vary inversely with the absolute pressure while the density varies directly with the pressure.

Charle's Law - If the pressure is kept constant, the volume of a gas will vary directly with the absolute pressure.

General Gas Law - Combined, Boyle's and Charle's Laws may be formulated:

$$\frac{P_1 U_1}{T_1} = \frac{P_2 U_2}{T_2} \quad \text{where } P_1 = \text{initial pressure (abs)}$$

$U_1 = \text{initial volume}$   
 $T_1 = \text{initial temperature (abs)}$   
 $P_2 = \text{final pressure (abs)}$   
 $U_2 = \text{final volume}$   
 $T_2 = \text{final temperature (abs)}$

Dalton's Law - The total pressure exerted by a mixture of gases is the sum of the pressures that would be exerted by each of the gases if it alone were present and occupied the total volume.

Henry's Law - The amount of a gas that will dissolve in a liquid at a given temperature is almost directly proportional to the partial pressure of that gas.

Effective Percentage - Any gas mixture has an absolute percentage of its components. In dealing with pressure, the number of molecules is increased with compression and as far as the body oxygen carrying mechanisms are concerned, the percentage might be said to increase. The quantity of gas per unit volume under pressure is expressed as though it were the percentage the body would experience at atmospheric pressure. When this is done, it is referred to as an Effective Percentage.

e.g. CO<sub>2</sub> of 3% has a minimal effect on the body. If the pressure is increased to 44.1 psi, the CO<sub>2</sub> has a marked and possibly lethal effect, as though it were 9% (3% x 3 atmos. = 9%). This is the effective percentage

Conversion of the various values obtained from instruments on board is desirable so that they will be expressed in similar terms. The CO<sub>2</sub> indicator reads, regardless of pressure, in absolute percentage; the oxygen meter (portable) is affected by pressure, thus reads as effective percentage. Conversion is based on the portion of Boyle's Law which states that density varies directly with the Pressure. In a submarine, the volume does not change, but the density may. Expressed:

$$P_1 C_2 = P_2 C_1 \quad \text{where } P_1 = \text{observed pressure}$$

$C_1 = \text{observed concentration}$   
 $P_2 = \text{final pressure}$   
 $C_2 = \text{final concentration}$

Examples:

- a. At 32" Hg, the O<sub>2</sub> was observed to be 20.5% on the oxygen meter.  
As this is an effective percentage, what is the absolute percentage of oxygen?

$$C_1 = 20.5\%$$

$$C_2 = X$$

$$P_1 = 32" \text{ Hg}$$

$$P_2 = 29" \text{ Hg (atmospheric)}$$

$$P_1 C_2 = P_2 C_1,$$

$$C_2 = \frac{P_2 C_1}{P_1}$$

$$C_2 = \frac{29 \times 20.5}{32}$$

$$C_2 = 18.6\% \text{ oxygen, actual percentage}$$

- b. At 28" Hg, CO<sub>2</sub> was observed to be 2.2%. It is desired to predict the effect on humans subjected to it, thus the effective percentage is desired.

$$C_1 = 2.2\%$$

$$P_1 = 29" \text{ Hg}$$

$$C_2 = X$$

$$P_2 = 28" \text{ Hg}$$

$$P_1 C_2 = P_2 C_1,$$

$$C_2 = \frac{P_2 C_1}{P_1}$$

$$C_2 = \frac{28 \times 2.2}{29}$$

$$C_2 = 2.12\% \text{ carbon dioxide, effective percentage}$$

N.B. - The same conversions must be made if expressed as partial pressures.  
In example (b), CO<sub>2</sub> partial pressure = 16.72 mmHg

$$C_2 = \frac{P_2 C_1}{P_1}$$

$$C_2 = \frac{28 \times 16.72}{29}$$

$$C_2 = 16.19 \text{ mmHg} = \text{p.p. of CO}_2 \text{ at reduced total pressure.}$$

### Expressing Concentration

There are several ways in which concentration may be expressed. The easiest way is by using terms of parts per million (ppm). This has no relationship to weight, but rather expresses simply the number of molecules

of the substance under discussion dissolved in a million molecules of diluent. It is related to percentage as may be seen from the following:

.000,001	=	0.0001%	=	1 ppm
.000,010	=	0.001%	=	10 ppm
.000,100	=	0.01%	=	100 ppm
.001	=	0.1%	=	1000 ppm

Another frequently used method of expressing concentration is in terms of mg/liter. This has the advantage of relating weight to volume allowing more rapid calculation of body uptake. It is possible to convert between ppm and mg/l with the following formulae:

$$a. \quad 1 \text{ ppm} = \frac{\text{molecular weight}}{1000 \times 24.45} \text{ mg/l}$$

$$b. \quad 1 \text{ mg/l} = \frac{24.45 \times 1000}{\text{molecular weight}} \text{ ppm}$$

The physiologic gases ( preponderately ) are expressed as partial pressures in mmHg. This is based on the ambient total pressure and the percentage. At standard pressure of 760 mmHg, the partial pressure of oxygen (20.95%) would be:

$$760 \times .2095 = 159.22 \text{ mmHg}$$

When the contaminant is a mist, dust, or fume (dispersed liquids or solids), the concentration must be on a weight/volume or a particle/volume basis.

#### Factors Governing Toxicity (Summary)

To summarize the totality of factors which must be considered in respiratory toxicity, one may list:

1. Concentration in air
  - a. Input vs. output
  - b. Stability of material
  - c. Exposure time
2. Physical state of the material in air
  - a. Gas
  - b. Aerosol
  - c. Dust or fume

3. Factors concerned with respiration
  - a. Normal minute volume
  - b. Conditions altering volume
4. Solubility in body fluids
5. Transportation within the body to site of where damage will occur
6. Tissue predilection
7. Mode of action - innate toxicity
8. Route and mode of elimination or toxicological deactivation

### Specific Toxicities

Without any attempt to be conclusive, the specific toxicological effect of a number of compounds are detailed. Selection is made on a basis of (1) materials commonly encountered in submarines; (2) those of general importance; or (3) those which illustrate actions of representatives of classes of compounds. Concern in this section will be only with physiological response and not with sensing or physical properties. MAC's given are those derived for use in industrial situations.

#### 1. Hydrogen Fluoride (MAC 3 ppm)

Evidence on necropsy of animals after repeated exposure shows damage to lungs, liver and kidneys suggestive of a process above that of usual irritant gases. Long-term exposure with retention of fluorine in bone has produced a generalized osteosclerosis. The highest concentration man can tolerate is 0.1 mg/l which produces smarting, a sour taste and conjunctival and respiratory irritation.

#### 2. Chlorine (MAC 1 ppm)

Damage from low concentration is limited to the nose and throat. Higher concentrations cause pulmonary oedema and broncho-constriction. A state of anoxia develops with classic signs. Acidosis can be a factor caused by dissolution of Cl in water hence, HCl. Chronic exposure leads to premature aging, bronchial disease, erosion of teeth, and increased susceptibility to tuberculosis. (Effects are similar with HCl)

#### 3. Ammonia (100 ppm)

An irritant and corrosive to the mucous membranes. Permanent damage to upper respiratory tract and bronchi, oedema, and reflex cardiac

cessation may result. Chronic exposure does not seem to be a problem as  $\text{NH}_3$  is rapidly converted to urea.

#### 4. Arsine

Arsine combines with haemoglobin causing haemolysis. The resulting rapidly developing anaemia may cause death. Pulmonary oedema may occur. Symptoms of anoxemia, frequently jaundice from haemolysis, and primary liver damage, and renal damage (with shutdown) may occur. Chronic exposure causes a compensated anaemia, albuminuria, haemoglobinuria and certain other bizarre symptoms.

#### 5. Phosphine

Does not cause haemolysis, but dyspnea, vertigo, oedema, convulsions, and death may result.

#### 6. Selenium

Nervousness, vomiting, dyspnea, tetanic spasm, shock. Effect is on CNS. Chronic exposure shows a distinctly 'garlicky' breath and possible hepatic damage and haemolysis.

#### 7. Sulphur Dioxide

An irritant gas. Low concentrations cause irritation of eyes, nose and throat. Pulmonary oedema may occur with increased concentration. Respiratory paralysis can supervene. Chronic exposure has shown nasopharyngitis, sensory changes, high urinary acidity and fatigue.

#### 8. Sulphuric Acid Mist

Choking, coughing, possible lung damage and dental erosion.

#### 9. Hydrogen Sulphide

Very insidious. Damage to body occurs when ability to oxidize the sulphides to sulphates or thiosulphates occurs. Systemic poisoning is then rapid with central nervous system damage, with hyperpnea and respiratory paralysis. With olfactory fatigue, severe poisoning may occur without warning. Sub-acute exposure causes irritation and affections of the eye and respiratory tract. Pulmonary oedema or broncho-pneumonia is

likely to follow exposures on the order of 700 ppm. With chronic exposure the eye develops a conjunctivitis.

#### 10. Carbon Disulfide

Predominant acute effect is narcosis and death from respiratory failure. Less severe exposure may result in vertigo, precordial distress, respiratory and gastrointestinal disturbances. With chronic exposure, one may develop amnesia, irritability, melancholia, mania, visual disturbances, impotence, gastrointestinal disturbances and other symptoms of central origin. Lung irritation and degenerative changes in the haemopoietic system have been reported.

#### 11. Oxygen

Under increased pressure of one atmosphere or more, convulsions occur, epileptiform in nature. With prolonged exposure to very high concentrations, a chronic respiratory irritation may develop. Concentrations below 16.0% are considered to lead to anoxia.

12-16%	Breathing and pulse increased, coordination slightly disturbed.
10-14%	Emotional upsets, abnormal fatigue, disturbed respiration.
6-10%	Nausea and vomiting, unconsciousness, and collapse with inability to move.
Below 6%	Convulsive movements, gasping respiration, and respiratory death.

#### 12. Ozone

Prolonged concentrations above 0.05 ppm may lead to pulmonary oedema. Eye, nose and throat irritation, chest cramps, headache and vertigo, fatigue, cough, lower blood pressure and continuous body pain occur.

#### 13. Nitrous Oxide

Asphyxiant and weak narcotic.

#### 14. Nitric Oxide and Nitrogen Dioxide

Asphyxia and pulmonary oedema which is not concurrent with exposure, but rather follows within a period of up to eight hours.

### 15. Carbon Monoxide

In competition with oxygen for haemoglobin, carbon monoxide has an affinity 300 times as great. This table is based on blood saturation:

0-10%	No symptoms
10-20%	Tightness over forehead, slight headache
20-30%	Headache and throbbing
30-40%	Severe headache, weakness, dizziness, dimness of vision, nausea, vomiting, and collapse.
40-50%	Increased probability of collapse
50-60%	Syncope, increased respiration and pulse, coma and convulsions, Cheyne-Stokes
60-70%	Coma and convulsions, depressed heart and lung action, possible death
70-80%	Weakness of pulse and slow respiration, respiratory failure and death.

Persons who recover from prolonged unconsciousness from CO poisoning may suffer damage to the heart, vascular system and viscera, but cerebral damage is the usual sequella leading to the "basal ganglia syndrome." Chronic effects are not different from acute. There is no substantiated evidence of long-term residua. Absorption and elimination of CO is solely through the lungs.

### 16. Carbon Dioxide

Acute poisoning is related to respiratory stimulation and problems are encountered when it acts as a diluent leading to anoxia. Long exposure to values of 1.5% are tolerated without distress, the only alteration being slight changes in the blood electrolytes; such changes are reversible within varying times after exposure.

### 17. Beryllium

Acute poisoning with initial symptoms of metal fume fever followed by extensive bronchiolo alveolitis. Some pneumonia-like syndromes have been reported. The mortality is fairly high. With chronic exposure there is a chemically induced pulmonary granulomatosis resembling Boeck's sarcoid. In chronic exposure, a slowly progressive disease with cachexia, dyspnea and ventral heart failure. Mortality is high. Skin lesions, granulomatous in nature, are seen following introduction of beryllium.

#### 18. Mercury

Mercury is a general protoplasmic poison. Intoxication from inhalation is characterized by a metallic taste, nausea, abdominal pain, vomiting, diarrhea, and cardiac weakness. Albuminuria occurs. Stomatitis and gingivitis with the mercuric sulfide line on the gums occurs. Recovery in milder cases occurs in 10-14 days. With chronic exposure, onset is delayed weeks to years. Psychic and emotional upsets are characteristic with agitation, fatigue and amnesia. A fine tremor is observed. A progressive course is anticipated. Neurasthenia is common as are optical lesions.

#### 19. Metal Fume Fever

Caused by the inhalation of zinc and other metallic fumes. The disease is found in welders and metal burners. Symptoms begin a few hours after exposure. They are a sweet taste, cough, fatigue, malaise, myalgia, chills, fever, and vomiting. Following profuse sweating, the temperature falls and recovery follows in a few hours. No known to be fatal. Some evidence of habituation.

#### 20. Aliphatic Hydrocarbons

Predominantly anaesthetic through octane. The margin between narcosis and death is narrow. Scattered reports of renal, hepatic and haemolytic anemia considered inconclusive. Levels below that causing acute symptoms are assumed to have no chronic effects. Neurasthenic reactions may occur and obscure and erratic central nervous system symptoms are seen including ataxia and incoordination.

#### 21. Unsaturated Hydrocarbons

As with aliphatic hydrocarbons but with more narcosis and greater margin of safety.

#### 22. Aromatic Hydrocarbons

In acute cases, the narcotic effect predominates. Symptoms may begin with exhilaration followed by fatigue, nausea and headache; with increased exposure, tonic-clonic convulsions, paralysis and unconsciousness occur. Death from respiratory paralysis. In chronic exposure, there is a profound anemia with decreased RBC, WBC's and low clotting ability with haemorrhage. Haemorrhagic manifestations.

### 23. Halogenated Hydrocarbons

Immediate acute effect is varying degrees of narcosis (choreiform). There is irritation of mucous membranes with coughing, sneezing, etc. In marked overdoses, should death from narcosis not occur, subsequent death from renal damage (shutdown, uremia) and hepatic injuries shown by gastrointestinal symptoms and jaundice may occur. Chronically, there is some variation in compounds but various neuritides, gastrointestinal and hepatic damage predominate. Also reported are degeneration of the brain and cardiac muscle as well as in haemopoiesis and altered metabolism.

### 24. Methanol

Primary hazard is ingestion. With inhalation one may see irritation, tinnitus, nystagmus, vertigo, dyspnea, nausea and vomiting, clouded vision, diplopia, blindness, pruritis and skin complaints.

### 25. Amyl Alcohols (example of higher homologues)

Vapors cause irritation of eyes and respiratory tract, headache, vertigo, dyspnea, nausea, vomiting and diarrhea. In severe cases, diplopia, deafness, CNS derangement, coma, glycosuria and metahaemoglobinemia.

### 26. Organic Acids

Generally damage is directly through burns.

### 27. Organic Esters

Initially conjunctival and respiratory irritation and narcosis. No apparent haematologic effect. Some gastrointestinal disturbances reported.

### 28. Aldehydes

Primarily irritant. Eyes and mucous membranes in moderate concentration. In high concentration pulmonary oedema may develop and in rare cases, asthmatic sequella.

### 29. Ketones

A narcotic action is encountered in very high concentration. Very few cases of ketone poisoning reported and none that were fatal.

### 30. Ethylene Glycol

Primary selective injurious effect on renal system with retention and uremia. The secondary effects of hepatic damage and CNS depression are only moderate. Acute death from narcosis; chronic effect is always renal. No recorded damage from prolonged small-dose exposure.

### 31. Phenol

The acute poisoning in man is characterized by action on higher nervous centers causing collapse. Most frequent routes of poisonings are by way of oral ingestion or through the skin. Chronic poisoning results in severe systemic disorders with gastrointestinal disturbances such as dysphagia, ptyalism, diarrhea, and anorexia. Central nervous disorders are common and death usually occurs when there is extensive damage to the renal and hepatic apparatus.

In defining damage to the body on the chronic subclinical level, one must consider the oftentimes extreme difficulty in demonstrating clinically that injury has occurred. The body is able to compensate for small alterations and return its status to near normal. It requires a fair amount of direct damage to the liver to overcome the hepatic reserve and develop positive evidence of impaired function; a low grade destruction of red cells can be compensated for by increased bone marrow activity; and the buffer systems in the blood maintain a relatively constant circulatory environment. Most alterations are reversible; some are not.

### 32. Synergism

When one is dealing with a wide variety of toxic materials in the same milieu, he must consider the possibility of enhanced (and in some cases reduced) physiological or toxicological effect from two or more of the materials acting in conjunction. The mechanisms are not known in complete detail but at least two are adequately documented: a. the competition for and blocking of detoxifying enzymes will have the effect of maintaining in the body an abnormally high concentration of the materials (e.g. cholinesterase inhibition) and b. anoxia-producing poisons may work at least additively to produce more severe symptoms (e.g. reduced O<sub>2</sub>-carrying capacity of haemoglobin will add to effect of a protoplasmic anoxic poison such as CN). The increased effect of CO and CO<sub>2</sub> is of interest in closed environments where both are always present. Ethyl alcohol potentiates the toxicological effect of almost anything. It is well to consider all atmospheric contaminants both singly and

as an aggregate in the evaluation of the effect of the respiratory environment on man.

Although not related to synergism in definition, there is another effect which can have much the same result. Activation of a compound in the atmosphere through oxidation, reduction, decomposition or other chemical alteration may create other compounds with different or more severe toxicological response. An oxide may be absorbed more rapidly or completely than its parent. The primary example of this phenomenon is that of freon which is a stable relatively non-toxic compound. When it is decomposed in the CO burner, hydro-chloric and fluoric acids are formed which are irritants. This reaction imposes the limit on acceptable levels of freon in the submarine atmosphere.

## SECTION II - Sensing for Airborne Contaminants

It is apparent that any attempt to control on a rational basis the introduction of potentially toxic materials in the air and to institute measures for removal of these and other naturally occurring materials, must be based on the knowledge of what these materials are and in what quantity they occur. The other requirement is knowledge of the level beyond which the contaminant must not be allowed to be maintained to prevent injury to man.

Occasionally the presence of a toxic material is determined through intricate and delicate laboratory techniques and a maximum permissible concentration (MPC) established on a basis of this information. When such an MPC has been established, and those in the field lack means to detect and quantitate these concentrations in their atmosphere, the situation is unsatisfactory. A large quantity of sensing equipment has been developed for industrial use usually with a range compatible with the probable industrial exposure. When a limit has been established for long-term continuous exposure 1-2 orders of magnitude below this limit, such equipment as is available is often of no value in the submarine problem. This indicates the fluid and dynamic state of the mechanics of atmosphere control. A development program constantly seeks to identify materials, to establish criteria, and to create sensing and control equipment. The fact that development of such control measures does not always keep pace with the need is understandable.

Within limits, the materials which are known to comprise the more significant airborne problems are susceptible to measurement. There is available equipment for wide spectrum sensing for rare toxic materials,

b. The paramagnetic effect of oxygen is utilized in detecting this gas. Oxygen has the property of altering magnetic permeation. With a glass dumbbell (in a magnetic field) supported on a quartz fiber, the oxygen containing gas is passed through the chamber. A force representing the balance between the torsion of the fiber and the magnetic field will cause deflection of the suspension. A small mirror mounted on the dumbbell magnifies the deflection by reflecting a beam of light. In calibration, a dividing prism distributes the light between two photo tubes. With torsion of the prism the light impinging on each photo tube is varied with a resultant inequality of electrical output proportional to the quantity of  $O_2$ . By balancing the current inequality, a value of  $O_2$  is generated on a dial.

c. Thermal conductivity is used to detect hydrogen. This gas has a property of rapidly conducting heat away from a heated source. A Wheatstone bridge is so balanced across heated filaments that there is no current flow in air. If two of the filaments are immersed in hydrogen, heat is conducted away from them more rapidly. A lowering of temperature alters the resistance of the filaments to current flow, hence, the balance of the bridge. The resultant current flow is measurable and with calibration is proportional to the amount of hydrogen present. This is a non-specific response. In the presence of helium (which exhibits the same phenomenon), the results are equivocal.

#### Portable Instruments

Portable instruments are a valuable adjunct to the atmosphere analyzer in atmosphere monitoring because:

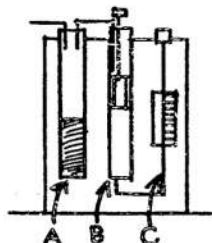
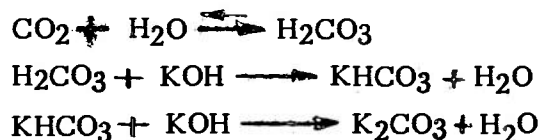
- a. They furnish an independent back-up system which is independently calibrated.
- b. They may be used in casualty situations when there may be loss of A-C power.
- c. They may be used to monitor in detail or in special studies for which the analyzer is poorly adapted.

In this group of instruments lies the versatility required for general evaluation of abnormal atmospheric conditions.

Principals of operation vary from system to system and are outlined as follows:

Oxygen Analyzer - Usually the Beckman unit is used. The principle is the paramagnetic effect previously discussed. Rather than electronically converting rotation of the suspension to a meter reading, the beam of light is read directly on a calibrated scale.

Carbon Dioxide Detector - The Dwyer CO<sub>2</sub> meter is generally used and is representative of the group of chemical indicators. Sample air is washed by bubbling through water in chamber (a), passing into the top section of (b). Agitation of the KOH in this chamber and mixing with the sample removes CO<sub>2</sub> from the sample through the following equations:



With pressures previously equalized (by venting) between chambers (b) and (c), the partial vacuum created in chamber (b) is converted to a proportional fall in chamber (c) by again equalizing pressure.

#### Tube Tests

The greatest capability for wide spectrum analysis of gases is inherent in the tube tests. In its simplest form, this sort of test requires a color producing (or changing) chemical reaction which is specific for the gas to be sampled. If the reaction is stable enough, the reactant is plated out on silica gel crystals or other granules and sealed in a small tube. Upon use, the seal is broken and a known quantity of sample is passed over the reagent. The estimation of concentration is made by color matching or measuring the length of the reactant column. There are a great many forms that such tests can take, depending on the manufacturer.

Within limits, this type of test is useful for two particular reasons: a. it allows for a sampling of a large number of substances with equipment requiring a minimum of space, and b. with low concentrations of various substances, a larger sample volume may be used. There are limitations involved in the sometimes involved and tedious sampling procedure, such as: the storage life of the tubes and question involving reliability, calibration, reproductability, and standardization among the sampling equipment produced by various manufacturers.

In general use on submarines there are several types of equipment including CO test equipment made by Mine Safety Appliances (MSA) or SafCoMeter, a general battery of tests for toxic materials using Draeger equipment and special tests designed by the U. S. Naval Research Laboratory.

It is worthwhile to indicate the classes of materials available in the Draeger system. A partial list follows:

Alcohol	Carbon Disulphide
Ammonia	Carbon Monoxide
Arsine	Chlorine
Benzene	Hydrocarbons
Benzene-Toluene	Hydrogen Sulphide
Carbon Dioxide	Mercury
Nitrous Gases	Sulphur Dioxide
Phosgene	Trichloroethylene
Prussic Acid	

In practice, the advisability of using this tube-type test must be judged by the situation presenting itself. If only an occasional spot check is made, it is likely to be negative. Obviously if a suspicious odor is present or personnel are complaining of symptoms, a complete check of the situation should be made.

In detecting this class of adventitious toxic materials, one will usually depend on means other than sampling for the initial indication of their presence. Peculiar odors, fumes, discolorations, etching of metal, smarting of eyes, coughs, and other symptoms will lead to suspicion and subsequent evaluation.

#### Miscellaneous Toxic Considerations

There is a group of random materials which can occur on submarines and, therefore, should be mentioned:

Monoethanolamine - May be recognized by its ammonia-like odor. Causes upper respiratory irritation and tearing. In large quantities can be very toxic and produce pulmonary oedema.

Ions - There are several sources of positive ions on board. The effects of ions are not well documented but are said to include cerebral irritability, decreased ciliary action and others. In general, negative ions are supposed to be good for people, positive ions bad.

There are a multitude of new development items currently employed on submarines, the specific and definitive toxicities of which have not been established. These are under study.

Paints form a large problem. Because of the aerosols and materials developed during drying (and setting up), the use of oil-based paints is interdicted while underway and for a period of weeks prior to leaving the yard. Water-based paints are, in general, superior to oil-based paints in this regard. These too generate toxic substances such as glycols. Specific paints, by name or Mil. Specification, are from time to time authorized for use. There seems to be no good gloss paint with a water base, but again, development is underway.

In summary, the state of the art for sensing atmospheric contaminants is far from perfect. There exists reasonably effective equipment for those components with which we are primarily concerned on a routine day in--day out basis. Others which might be expected in an intermittent or emergency situation are covered at least partially by tube-type sample systems.

## References

It is worthwhile to carry on board a limited number of reference texts in toxicology. Those recommended by the Officer in Charge, Navy Toxicology Unit are:

1. Industrial Hygiene and Toxicology - Vol. I: General Principles. Clayton, et al. 1958, Inter-Science Publishing, Inc., New York.
2. Dangerous Properties of Industrial Materials - Sax, et al. 1957, Reinhold Publishing Corp.
3. Clinical Toxicology of Industrial Materials - Acute Poisoning. Gleason, et al. 1957, Williams & Wilkins.

### SECTION III - Equipment for Atmosphere Control

It has been stated at one time or another that an atmosphere approximating the composition and purity of natural air is our goal. On the assumptions that our atmosphere is ideal for man and that we are not talking about "pure" Los Angeles smog, it is an acceptable statement. By whatever definition chosen, we do desire pure air in submarines. Ultimate purity is not possible in a changing situation where there is a constant introduction of new material. In fact, from the nature of any equipment for removing specific matter from the air, its efficiency will fall off as the quantity of the material becomes less until finally the curve of concentration becomes asymptotic. Hence, a balance must be struck between the desire to have pure air, the known effects of contaminants at various concentrations and the ability of engineers and chemists to design equipment for removal of any given contaminant.

One must also scrutinize the equipment lest of itself it contributes some type of contaminant to the problems of pure air. It is possible in solving one problem to create new and possibly more serious ones. A situation has arisen on several occasions where faulty operation of equipment, including purifying equipment has resulted in release of noxious gases into the air.

#### Factors Present Which Contribute to Air Purification

It is in many ways fortunate that one does not have to depend solely upon designed equipment to aid in air purification. There are several factors which by design or fortune aid in clearing the air:

1. Reversion to non-toxic material - some materials which are noxious are unstable in air and will through oxidation or reduction revert to a less toxic form, e.g. ozone, created by electrical arcs or u-v light is unstable and reverts to  $O_2$ .

2. Air conditioning- many water soluble materials are condensed out of the air along with water on the cooling coils in the air conditioning plant. Condensate water is ultimately pumped or blown overboard. Air conditioning capacity has grown from a scant six tons in World War Two to an amount in excess of one hundred tons on new submarines.

3. Ventilation - some toxic effects are the result of accumulation within a confined space. If a concentration in the local area can be dispersed throughout the volume of the ship, dilution can reduce the concentration, hence the hazard to negligible values.

4. Inert filters - dust particles can function as nuclei for aerosols and other finer particles. By mechanically filtering out dust, some airborne toxic materials are removed.
5. Activated carbon filters - various hydrocarbons are selectively adsorbed by carbon filters. Use is limited for, with saturation, competition occurs and more toxic forms are selectively desorbed.
6. Electrostatic precipitator - a valuable piece of equipment. It removes aerosols and particulate matter which can be ionized (vide infra).
7. Carbon monoxide burner - oxidizes CO and other materials by combustion (vide infra).
8. Carbon dioxide scrubber - removes CO<sub>2</sub> by a cyclic absorption in an amine (vide infra).
9. Man - The human body forms an excellent biological system for collection and detoxification of many agents, providing concentrations and innate characteristics of the materials are not such as to cause poisoning. The continuous detoxification by one hundred people will help prevent the concentration of many mild contaminants from building up to poisoning levels.
10. Control program - Prophylaxis, where possible, is the best cure for contamination. Programs designed to prevent or limit the introduction into the submarine of known toxic solvents and the like can reduce hazards greatly.
11. Manifold breathing - Some submarines now have a system for mask breathing, taking pure air from the 3000# banks through reducers and demand valves. This allows continued submergence in emergency situations where fumes or gases from fire or other mishaps reach intolerable levels. Designed to allow ship control and individual survival for many hours.
12. Surface ventilation - a last resort under tactical conditions. Use of snorkel ventilation is a partial compromise. The closed environment envisioned for space flight will not have this refuge.

## Oxygen

There are several sources of oxygen available for submarines and several concepts under development. Oxygen is utilized for all purposes including oxidative processes and combustion (smoking, CO burner) at a

rate of CA. 0.85 cu.ft./hour/man. Over a period of months, the requirement becomes a significant one. At the present time oxygen sources are:

1. Oxygen banks - in general use. Oxygen is stored in large flasks outboard under high pressure. Through reducers, oxygen is bled into the vessel at a rate consistent with its use. A positive and sure system but limited by volume of O<sub>2</sub> available.

2. Oxygen cylinders - emergency O<sub>2</sub> in flasks throughout the vessel. Of value primarily to individuals. It should be reserved for emergency medical use.

3. Air banks - By cycling air into the banks (compressors) and releasing new air from the banks, a relatively small quantity of oxygen may be realized. This now has very little general application.

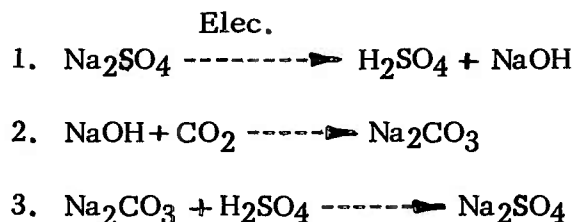
4. Oxygen candles - By storing and using on board, candles give an added oxygen capacity. Similar in principle to the OBA candles, a catalyzed chlorate when burned yields O<sub>2</sub> (and salt). Chlorine may be present but a candle is being developed which should give negligible yields of this gas. Principal problem lies in the bulk of candles which means a storage problem.

5. Oxygen generator - Coming into use on submarines is the generator. This equipment creates oxygen and hydrogen by hydrolysis of sea water. The hydrogen is, of course, an explosive hazard and must be kept under control. As H<sub>2</sub> is generated, it is pumped into a hold tank and ultimately blown overboard. This system costs power but is valuable for a long-term supply. The system is usually supplemented and backed-up with stored oxygen.

6. Partial pressure - It is possible by increasing pressure within the submarine to increase the partial pressure, e.g. 10% oxygen at 29.4 psi (2 atmos) is equivalent to 20% (effective). This is not an approved technique. Prior to surfacing, pressure must be reduced and there is a period of a few minutes during which anoxia can occur.

There are several systems under study and development which attempt to make O<sub>2</sub> available from CO<sub>2</sub>. This approach would have the dual benefit of yielding oxygen and reducing CO<sub>2</sub>. Examples of the areas in which promise lies include:

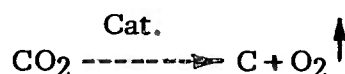
1. The sulphate cycle - This embraces a set of chemical reactions which must be incorporated into a mechanical-electrical system.



2. Algae - The use of a biological system (plant) which utilizes the photosynthetic conversion of  $\text{CO}_2$  to  $\text{O}_2$  and various organics. This process is a promising approach but one which has many problems in long-term strain propagation.

3. Sodium superoxide - A static chemical reaction wherein  $\text{Na}_2\text{O}_2$ , being unstable, can be made to yield  $\text{O}_2$ . The resultant base ( $\text{NaOH}$ ) is then used to absorb  $\text{CO}_2$ . Preliminary studies at ACEL show some promise on a weight/man/hour basis necessary.

4. The ideal "black box" solution is also being sought. This would employ a catalyst which would have the ability to cause the following reaction to occur:



Unfortunately, this catalyst is not known.

## Carbon Dioxide

The removal of this physiological gas is necessary. It has been a problem associated with submarines and recognized as such for a great many years. Control has not been feasible (nor necessary) except in emergency situations so development has not been pushed. With the long-term capability of nuclear submarines and, to some extent, earlier problems on ASSP5 (personnel submarines), a system was necessary to maintain a constant removal capacity. At present, there are available:

1. Use of bases. Any one of several bases are useful in this regard, all entering the basic equation  $\text{aOH} + \text{H}_2\text{CO}_3 \text{ -----} \text{aHCO}_3 + \text{a}_2\text{CO}_3 + \text{H}_2\text{O}$ . Originally using soda-lime, it is now possible through hoppers designed for good efficiency to use  $\text{LiOH}$  and possibly  $\text{KOH}$  or  $\text{NaOH}$ . These materials are useful primarily under emergency conditions.

2.  $\text{CO}_2$  scrubber. The current mainstay of the  $\text{CO}_2$  removal effort, this equipment uses a specific characteristic of monoethanolamine, to wit, at low temperatures it will absorb  $\text{CO}_2$  and at high temperatures release it.

This is designed into a system, exposing low temperature MEA to ship's air, pumping it through a heat exchanger into a heating chamber. Here the CO<sub>2</sub> is driven off, collected and pumped overboard. The MEA is then pumped through the heat exchanger, cooled and returned to the exposure chamber to begin the cycle again. There are two machines on each submarine, each capable of maintaining required levels. The machines require meticulous surveillance during operation both to assure performance and to prevent the MEA from being carried over into the ship's ventilation system. The MEA is toxic to man. Special equipment for sensing and measuring concentration has been developed and is available on submarines using the scrubber. The system loses efficiency markedly when the ambient CO<sub>2</sub> level is low.

### Carbon Monoxide

The sources of carbon monoxide on submarines are primarily smoking, cooking, drying paint, lagging and the like. It's known toxicity and synergism with CO<sub>2</sub> make it absolutely necessary to remove it from the air. The usual result of an increased level in the submarine is a rash of people complaining of "splitting headache." Removal is accomplished with a single piece of equipment.

The CO burner was originally designed during World War Two as a hydrogen burner. The chronic problems of H<sub>2</sub> generation with its explosive hazard was alleviated by burning the gas as it was generated.

Using hopcalite as a catalyst, CO enters the chamber and is converted to CO<sub>2</sub>. The CO<sub>2</sub> is then removed by the scrubbers. CO levels may be maintained within prescribed limits by using one or two of the units. Air entering the burner must be prefiltered lest the catalyst become clogged and ineffective. Other contaminants in the air are also oxidized by the burner which contributes generally to purity of the air. Freon - 12, on the other hand, is dissociated from HCl and HF as it passes through the heated chamber. This has a destructive effect on the metals in the system and is not considered to be acceptable for people. The incorporation of marble chips (carbonates) in the catalyst helps reduce the over-all problem.

### Aerosols

A large proportion of the aerosols in submarines derive from cigarette smoke and cooking vapors as well as from paints and other sources. Removal is accomplished primarily through the use of the electrostatic precipitator.

This equipment ionizes particles or aerosols upon entry then passes the ions between plates on which 14,000 v. are impressed. This field causes plating out of the ions. Periodic cleaning of the plates is necessary for efficiency, for large quantities of sludge accumulate particularly in some areas such as the galley where the bulk of aerosols from cooking (and especially frying) arise. This equipment is very effective. Present capacity is 1200 cu. ft. and plans to increase this to a capacity of thousands of cu. ft. are underway.

### Conclusion

For the major problems encountered when attempting to furnish a submarine with a constant supply of pure air, there are workable solutions. The solutions at present all have certain drawbacks, but have a salient feature, they work. The subtle problems of low-grade chronic toxicity are unexplored, not only in their toxicity under these conditions, but also in their detection and removal.

Despite the fact that man can function as a detoxification plant, there is some question as to whether he should be designed into the system in this capacity.